

Effect of Sodium Bicarbonate as Blowing Agent on Production of Epoxy Shape Memory Foam using Aqueous Processing Method

(Kesan Natrium Bikarbonat sebagai Agen Tiupan kepada Penghasilan Buih Ingatan Bentuk Epoksi menggunakan Kaedah Akueus)

MUHAMMAD SYAZWAN FAUZI, DU N.U. LAN*, HAKIMAH OSMAN & SUPRI A. GHANI

ABSTRACT

Epoxy shape memory foam (ESM) was produced by an advanced aqueous method. Mixture of epoxy, sodium bicarbonate, hardener and ammonium chloride was premixed and emulsified in distilled water by using high speed stirring (at 1200 rpm). The content of sodium bicarbonate used was 5, 10, 15 and 20 phr. Besides that, ammonium chloride was used (based on stoichiometrical content) to also function as acidifying agent in initiating the decomposition process of sodium bicarbonate at lower foaming temperature. The foam morphology was observed using SEM. It was found that higher sodium bicarbonate produced more porosity, more cell size, thinner cell wall and more cell interconnection. Epoxy shape memory foam with 10 phr of sodium bicarbonate exhibited good shape memory property and better compression set. Shape memory behaviour was measured by the recovered time of the transformed sample to its original shape.

Keywords: Aqueous method; compression set; compression test; epoxy shape memory foams; sodium bicarbonate

ABSTRAK

Buih ingatan bentuk epoksi (ESM) telah dihasilkan dengan kaedah akueus. Campuran epoksi, natrium bikarbonat, pengeras dan amonium klorida telah dipracampur dan diemulsi di dalam air suling dengan menggunakan kelajuan pengacau yang tinggi (pada 1200 ppm). Kandungan natrium bikarbonat yang digunakan ialah 5, 10, 15 dan 20 bsr. Di samping itu, amonium klorida telah digunakan (berdasarkan kandungan stoikiometrik) juga berfungsi sebagai agen pengasidan dalam memulakan proses penguraian natrium bikarbonat pada suhu lebih rendah. Morfologi buih telah diperhatikan dengan menggunakan SEM. Didapati bahawa natrium bikarbonat yang lebih tinggi menghasilkan lebih keliangan, saiz sel yang lebih, dinding sel yang nipis dan sambungan antara sel yang banyak. Buih ingatan bentuk epoksi dengan 10 bsr natrium bikarbonat menunjukkan ingatan bentuk yang baik dan set mampatan lebih baik. Tingkah laku ingatan bentuk untuk berubah kepada bentuk asal diukur masanya.

Kata kunci: Buih ingatan bentuk epoksi; kaedah akueus; natrium bikarbonat; set mampatan; ujian mampatan

INTRODUCTION

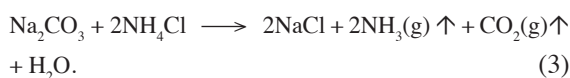
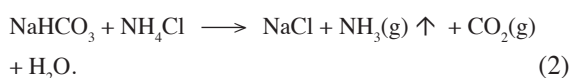
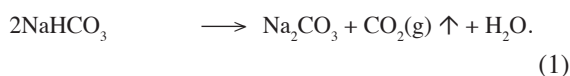
Polyamide epoxy adduct is a product of the reversed ratio of polyamide –epoxy ratio, in which excess stoichiometric polyamide is used. This provides a flexible and three-dimensional crosslinked polymer. The increase in flexibility of the obtained polymer is due to the reduction of the crosslink density via the use of excess hardeners. Free polyamide molecules (primary amide) react with epoxy groups twice faster than the second functional amide groups left on the reacted polyamide molecules, because free polyamide molecule has more mobility and has less steric hindrance. The result of this reaction is the formation of less three dimensional network crosslinks and short polymer chains. Versamids is a type of polyamide hardener for epoxy, which has a long polymer chain and is produced from vegetable oil. It has been used as hardeners-cum-flexibilisers for epoxy resin (Abu Bakar et al. 2009). It is believed that the reduction in crosslink density could allow the foaming process to occur better in the mixture and obtain homogeneous foam. Therefore, the polyamide

– epoxy adduct was exploited in this project to produce a flexible foam.

Shape memory foam (SMF) has a capability to memorize its shape as well as recover to its original shape from external stimuli such as heat, light, pH and moisture (Santosh Kumar et al. 2012). SMF has been used in many other applications such as in construction, electronics, textiles, transportation and medication (Zunaida et al. 2007). In this study, shape memory property is aimed for the recovery ability to its original shape inflicted by causing an external mechanical deformation. It is different with permanently deformed in plastic or elastic recovering response. The shape recovery occurs in a period of time after releasing the applied load. In this way, the shape memory property could be related from the foam structure. Foam cell interconnection and porous cell wall are the main contribution factors to the shape memory property of polymeric foam. Aqueous preparation process is a suitable method to form these morphology features for epoxy foam. Water works as emulsion medium for polymer droplets

when the emulsion system is stirred at high speed rotation. Moreover, water in this advanced aqueous method also acts as a pore template besides the use of blowing agent. It means that the water will be trapped inside the polymer's emulsion during homogenization and results the porosity in the polymer after cured (Lan et al. 2011).

Sodium bicarbonate (NaHCO_3) is one of the most common and green blowing agent. It produces carbon dioxide (CO_2) and water (H_2O) when heated as shown in (1) (Bakirtzis et al. 2009). In this investigation, ammonium chloride was also used to promote and accelerate the blowing process of sodium bicarbonate via (2) and (3). The foaming process of epoxy foam is relatively simple and economical (Alonso et al. 2006).



EXPERIMENTAL DETAILS

MATERIALS

Diglycidyl ether of bisphenol A (DGEBA, epoxy equivalent weight, EEW 182 – 192 g/eq), was provided by Euro Chemo Pharma Sdn Bhd, with a commercial code of DER 331. Hardener grade A 062 was also supplied by Euro Chemo Pharma Sdn Bhd. The sodium bicarbonate was obtained from Kasihku Marketing Sdn. Bhd. Ammonium Chloride with molecular weight of 53.49 g/mol was obtained from HmbG chemical, Hamburg, Germany. Distilled water was prepared in house and used for all the experiments.

PREPARATIONS OF THE FOAM

The samples were prepared by mixing blowing agent into epoxy resin with appropriate content. The mixture was stirred for 2 min using overhead mechanical stirrer at the rotor speed of 300 rpm. Polyamide was added into

the mixture with required proportion. The mixture was continuously stirred for another 2 min at 300 rpm. After that, distilled water was charged into the mixture and this was followed by increasing the speed of mechanical stirrer to 1200 rpm. Lastly, ammonium chloride was added and stirred at 600 rpm for another 2 min. The amount of ammonium chloride calculated base on the amount of sodium bicarbonate (Table 1). The mixture was then casted into the mould with the dimension of $110 \times 110 \times 25$ mm and cured at 80°C for 1 h. Then, the cured foam was taken out of the mould. The formulations of epoxy foams are shown in Table 1.

LEACHING PROCESS

Reaction between sodium bicarbonate and ammonium chloride would produce sodium chloride. So, leaching process was needed in order to wash out the NaCl salt. The process started by immersing the foam into distilled water of 90°C in a glass container placed inside a water bath for an hour. The leaching process has also functioned as a post-cure process for the epoxy SMF. After the leaching process, the samples were dried in the oven and ready for testing and characterization.

CHARACTERIZATION

Morphology Scanning electron microscopy (SEM) was used to study the morphology of the foam. SEM was done using model JEOL JFC 6460 LA. The sample was sputter coated by gold-palladium using a sputter coater (Polaron-SC7620) for 90 s to prevent surface charging.

Shape Memory Testing The samples were cut into rectangular shape with dimension of $10 \times 10 \times 50$ mm. They were twisted 180° from its original shape and released immediately. The duration taken by the sample to transform back to its original shape was recorded as recovery time.

Flatwise Compression Compression strength was determined using ASTM C365 using Instron machine. The speed was 10 mm/min. The dimension used was $50 \times 50 \times 25$ mm. The sample was compressed until 75% of compressive strain.

Compression Set The compression set was carried out according to ASTM D 3575 using two flat plates that parallel

TABLE 1. The nomination and formulation of epoxy shape memory foam

Nomination	E:P ratio	Epoxy (phr)	Polyamide (phr)	Blowing agent NaHCO_3 (phr)	Distilled water (phr)	Ammonium chloride (phr)*
		(100 phr)				
ESM1	1:3	25	75	5	300	3.2
ESM2	1:3	25	75	10	300	6.4
ESM3	1:3	25	75	15	300	9.6
ESM4	1:3	25	75	20	300	12.76

ESM: epoxy memory shape foam, E: epoxy, P: polyamide; (*) based on the stoichiometric of reaction 3

and fixed to each other by using clamps. The sample was compressed to 50% strain and kept between plates with a predetermined distance that can be adjusted using metal gaskets for 23 h at room temperature. The dimension used was $50 \times 50 \times 25$ mm. The compression set value was calculated by the following equation:

$$C_d = \frac{t_o - t_f}{t_o} \times 100,$$

where C_d is compression set expressed as percentage of the original thickness, t_o is the original thickness (mm) and t_f is thickness of the specimen after the recorded recovery period (mm).

RESULT AND DISCUSSION

FOAM MORPHOLOGY VIA SEM OBSERVATION

It can be seen from the foam morphology that high blowing agent content produced more porosity and more interconnection between neighbouring cells (Figure 1).

The foams are considered as open cell foams with large cell size and porous cell walls. Comparatively, ESM2 has smaller cell size and porous cell wall; while ESM3 and ESM4 possessed larger cell size and more cell interconnection. The interconnection between cells is lower in ESM4 compared with ESM3. This could be explained that the excess of blowing agent during foaming in ESM4 produced larger air pressure at early curing stage, when there were less of initial crosslink in epoxy-polyamide. Hence, the pores boundaries would coalesce to others resulting in big cell size with less pore and thin cell wall foam.

SHAPE MEMORY PROPERTIES

Reversed ratio used between epoxy and polyamide had produced polyamide-epoxy adduct which was flexible, soft and able to be twisted. The rectangular ESM foam was twisted and released as shown in Figure 2(b) from its original shape as shown in Figure 2(a). After loading release, the ESM foam started to recover (Figure 2(c) and (d)). It could be said that shape memory property can be considered as the presence of delayed elastic

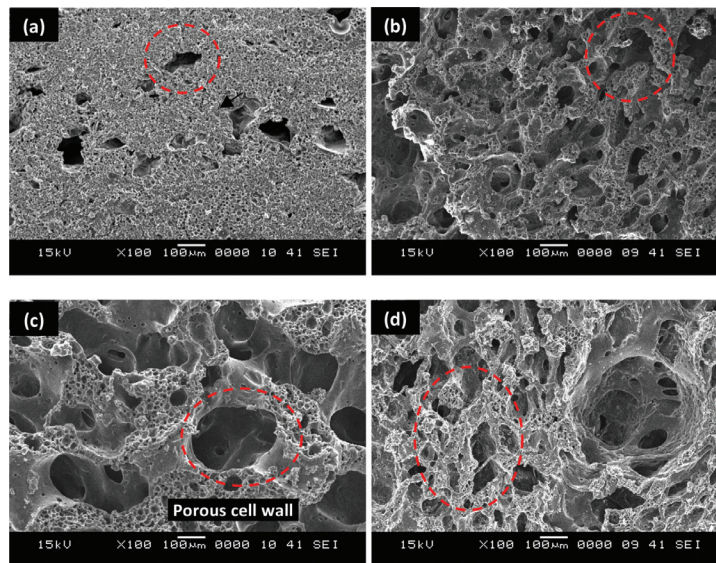


FIGURE 1. Morphology of epoxy shape memory foam (a) foam cell of ESM2 at 100× magnification (b) foam cell of ESM4 at 100× magnification (c) porous cell wall of ESM2 and (d) solid cell wall of ESM4 (200×)

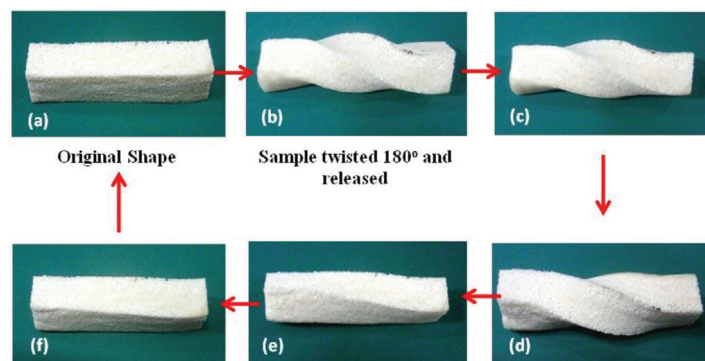


FIGURE 2. Recovery mechanism of epoxy shape memory foam

characteristic. Total recovery was possible with the help of crosslinking network available in ESM. However, the porous cell wall caused the longer time for the foams to recover back to their original shape because of their porosity and interconnection between cells, which cause the elasticity characteristic more difficult to transfer within the sample. The internal shear stress was released first and the twisted deformation of the sample was reduced twisting until 90% from its original shape as shown in Figure 2(e) and 2(f). The time taken for complete recovery was recorded as shown in Table 2. So, it could be concluded that the long chain of polyamide between crosslink allowed the ESMs to be bent and deformed and low crosslink density helped the ESMs be able to recover; while the foam structure exhibited the shape memory property.

FLATWISE COMPRESSION PROPERTIES

Figure 3 shows the compressive strength of ESM at 50% of compressive deformation. It was found that ESM1 exhibited the highest compression strength compared to these of others. This was expected because the low blowing agent content of 5 phr in ESM1 induced low porosity in the foam. It is well known that compressive strength and modulus decreases with increase in porosity (Hadi et al. 2011). In addition, more porosity on the foam cell wall could provide more inter-connection between foam cells, which can also produce more porosity on the cell wall. It can help in giving more space for more deformation between cells without deformation or breakage the foam cell and matrix. Thus, lower load will be applied to compress the ESM2 foam compared to ESM1.

Nevertheless, having higher blowing agent content, ESM4 exhibited higher compression strength and modulus

compared to ESM3. The reason could be due to the ESM4 had less cell interconnection compared to ESM3 as shown in Figure 1(c) and 1(d). At higher 10 phr of blowing agent dosage, the gas decomposed was too much that the green crosslink matrix could not hold the excess expanding gas. More cells are coalesced and less homogeneous size, which was also observed in LDPE foam reported by Zunaida et al. (2007). In contrast, the un-decomposed of excess blowing agent could also be a reason of increment in compression strength and modulus. These un-decomposed blowing agents would change their role to be as filler and stiffen the foam matrix. The assumption was also supported by the very similar compression stress before 50% strain of ESM3 (15 phr) and ESM4 (20 phr) but turned to be significant when the compression reached 75% strain and if compression modulus is taken into consideration as shown in Figure 4 and Table 2. The compression curves started to increase gradually due to the in-contact of among cell wall throughout the foam (Lorna 2005). The higher load required to compress ESM4 deflected at higher 50% strain could be an evidence of stiffer foam matrix reinforced by un-decomposed blowing agent.

COMPRESSION SET

Figure 5 shows similar effect of blowing content on compression set to compression results, wherein ESM2 (10 phr of blowing agent) exhibited the best compression set result, further increase in blowing agent caused poorer compression set of ESM3 and ESM4. The optimum foam structure of ESM2 such as high porosity, homogeneous cell size and porous cell wall showed significant result of 100% recovery. The advantage of foam structure of ESM2 was easily to be compressed. Table 3 shows that, it

TABLE 2. Recovery time taken from twisted samples to its original shape (seconds)

Samples	ESM1	ESM2	ESM3	ESM4
Recovery time (seconds)	58	76	54	49

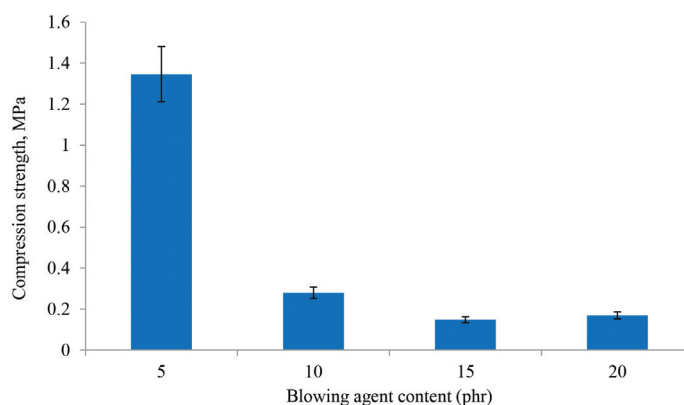


FIGURE 3. Effect of blowing agent on compression strength of ESM foam

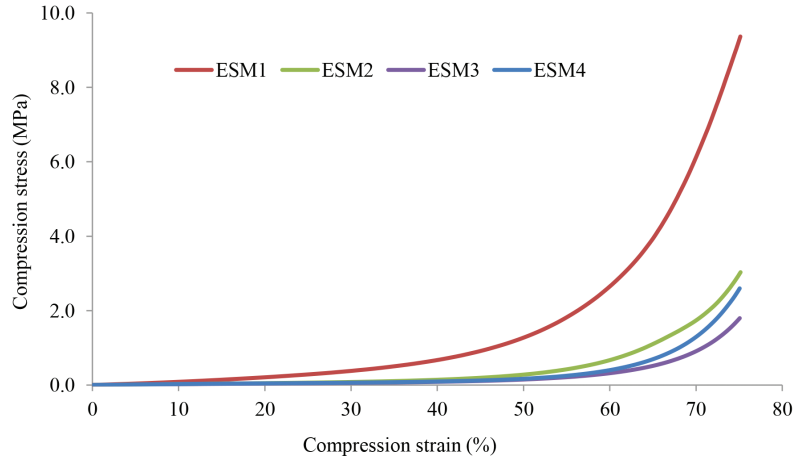


FIGURE 4. The flatwise compression stress and strain curves of ESM at different blowing agent content

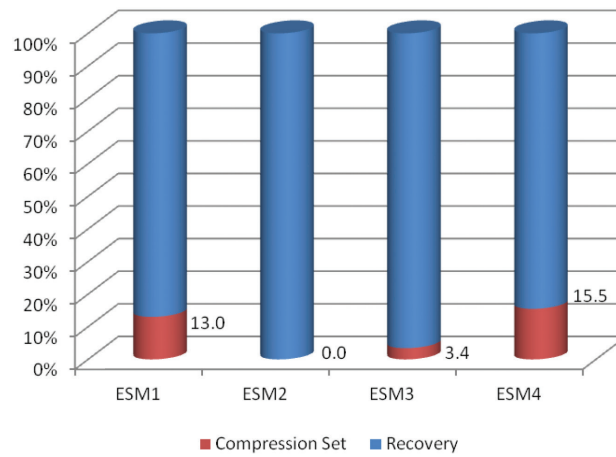


FIGURE 5. The compression set graph of 4 different ratios of ESM at room temperature

TABLE 3. Flatwise compression properties of ESM at different blowing agents content

Samples	Compression stress at 10, 25, 50 and 75% strain (MPa)				Modulus (MPa)
	10	25	50	75	
ESM1	0.081	0.291	1.346	9.28	1.47
ESM2	0.025	0.064	0.28	2.92	0.33
ESM3	0.022	0.048	0.148	1.796	0.25
ESM4	0.029	0.053	0.169	2.597	0.29

only required 0.28 MPa compression stress to compress the ESM2 to 50% strain, which is the compressive strain requirement in compression set test. It means there was a less arrangement and deformation in the ESM2 structure during compression set. It results no rupture occurred after compression set, and the foam is able to recover 100%. Due to high porosity, ESM3 and ESM4 cannot recovered fully because the cell wall easier to be cracked and crack-propagated and damaged.

CONCLUSION

Epoxy shape memory foam was successfully prepared using the proposed aqueous method. It was found that 10 phr was the optimum blowing agent content to produce a good shape memory foam, low compression and 100% recovery after compression set. Shape memory occurred through low level of crosslink density of polyamide-epoxy adduct and the characteristic of the foam cellular structure. Optimum interconnection between cell, porous cell wall

and homogeneous cell size are the key points for shape memory and compression set properties.

ACKNOWLEDGEMENTS

The authors would like to acknowledge University Malaysia Perlis - UniMAP for providing short term grant (grant no: 9001-00336) and research facilities that has made this work possible.

REFERENCES

- Abu Bakar, A., Lan, Du N.U., Azahari, B. & Ariff, Z.M. 2009. Production of novel epoxy micro-balloons. *Materials Letters* 63: 827-829.
- Alonso, M.V., Auad, M.L. & Nutt, S. 2006. Short-fiber-reinforced epoxy foams. *Composites: Part A* 37: 1952-1960.
- Bakirtzis, D., Delichatsiosa, M.A., Lioukakis, S. & Ahmed, W. 2009. Fire retardancy impact of sodium bicarbonate on ligno-cellulosic materials. *Thermochimica Acta* 486: 11-19.
- Lan, Du N.U., Abu Bakar, A., Azahari, B., Ariff, Z.M. & Chujo, Y. 2011. Porous epoxy microparticles prepared by an advanced aqueous method. *Materials Letters* 65: 1655-1658.
- Hadi, A., Baghshahi, S., Emadi, R. & Naghavi, S. 2011. Different pore size alumina foams and study of their physical and mechanical properties. *Proceedings of the 2011 IAJC-ASEE International Conference*. Paper 132, ENG 108.
- Lorna, J.G. 2005. Biomechanic of cellular solids. *Journal of Biomechanic* 38: 377-399.
- Santhosh Kumar, K.S., Biju, R. & Reghunadhan Nair, C.P. 2012. Progress in shape memory epoxy resins. *Reactive & Functional Polymer* 73: 421-430.
- Zunaida, Z., Zulkifli, M.A., Hwa, T.L. & Sipaut, C.S. 2007. Effect of foaming temperature on morphology and compressive properties of ethylene propylene diene monomer rubber (EPDM) foam. *Malaysian Polymer Journal* 2(2): 22-30.

School of Material Engineering
Universiti Malaysia Perlis (UniMAP)
Kompleks Taman Muhibah, Jejawi 2
02600 Perlis
Malaysia

*Corresponding author; email: uylan@unimap.edu.my

Received: 15 January 2014

Accepted: 15 November 2014